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Effects of the Support and Sintering on Hydrogen Uptake of Nickel Supported on Porous Vycor Glass

This note examines why the hydrogen uptake of nickel adsorbed on porous Vycor glass (Ni/PVG[1]) varied peculiarly with changes in reduction conditions.

The grain size of the PVG was 80–100 mesh. Its surface area and its pore diameter were determined by nitrogen adsorption to be 419 m^2/g and 2 nm, respectively. Nickel, 3.92 wt%, as metal adsorbed on PVG was washed with water and then was reduced by passing hydrogen at a rate of 100 cm^3/min in a quartz glass tube. Hydrogen uptake was measured at 298 K while keeping the pressure at 150 Torr (2). The BET surface area and the pore size distribution was then calculated from the nitrogen adsorption experiment. Crystallite size was measured directly from TEM micrographs. The amount of nickel dissolution was calculated from the concentration of nickel in the dilute nitric acid in which Ni/PVG was soaked for 2 days.

The pore size distribution decreased substantially when the PVG heated at 1073 K for 3 h as shown in Fig. 1. On the other hand, the pore size distribution of Ni/PVG became bimodal with an enlargement of pores because of dissolution of some pore organization during nickel adsorption (*1*). The pores of Ni/PVG were not closed; however, the maximum of numerical mean diameter of crystallites was 11 nm (Fig. 2), bigger than the pore size of PVG.

Hydrogen uptake decreased rapidly between 21 and 23 h at 773 K (Fig. 3) with a decrease in the BET surface area (Fig. 4) in spite of the approximately constant crystallite size. This showed that the decrease in BET surface area significantly depressed the hydrogen uptake. For this effect, hydrogen uptake was less at 973 K than at 873 K after 6 h. Hydrogen uptake did not increase even for longer reduction time over 873 K. In addition to a decrease in BET surface

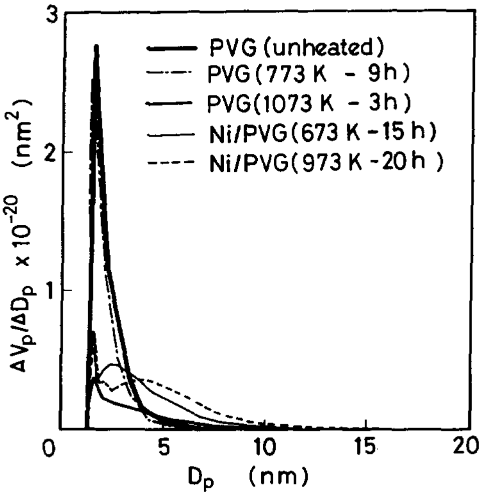

FIG. 1. Pore size distributions of unheated PVG, heated PVG, and Ni/PVG.

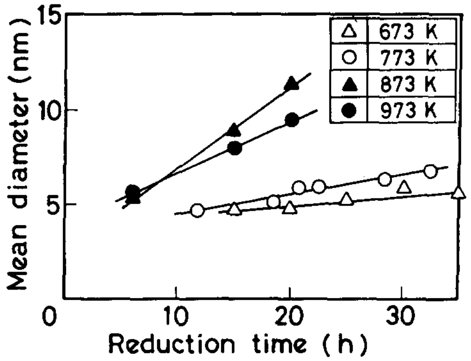

FIG. 2. Numerical mean particle diameter of dispersed nickel on surface of Ni/PVG.

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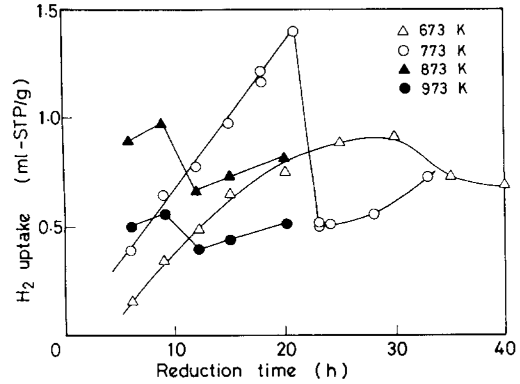

FIG. 3. Hydrogen uptake of Ni/PVG reduced at 673, 773, 873, and 973 K.

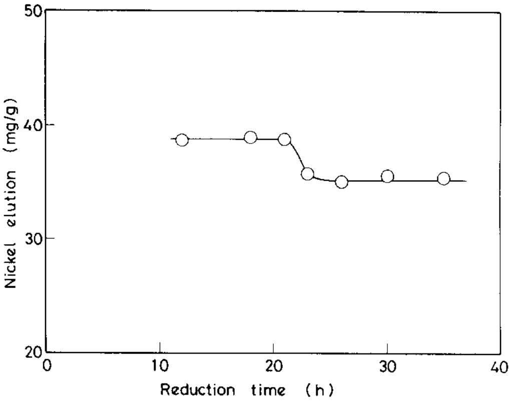

FIG. 5. Nickel dissolution from Ni/PVG into dilute nitric acid.

area of the support in the initial stage, another reason for the decrease in hydrogen chemisorption may be fast crystallite sintering of nickel.

As shown in Fig. 5, the amount of nickel dissolution decreased simultaneously with the hydrogen uptake in Fig. 3 and BET surface area in Fig. 4. These results show that decrease in hydrogen uptake was due to burial of crystallite under the support, not due to interaction between metal and support such as SMSI. It is considered that 9.6% of the crystallites that correspond to the decrease in nickel dissolution was completely buried with most of the buried crystallites being partly exposed. Elmer (*3*) has discussed the interaction of the siloxane groups on adjacent pore walls that causes rapid pore closure and the accumulation of strain in the pore structure that causes viscous flow of the support on a local level. This contraction mechanism can explain the burial and that the surface area decreased sooner at a higher temperature as shown in Fig. 4.

It is necessary to prevent such a burial for high dispersion. The optimum condition of reduction was at 773 K after 21 h and gave the considerably high dispersion of 18.7% (*2*).

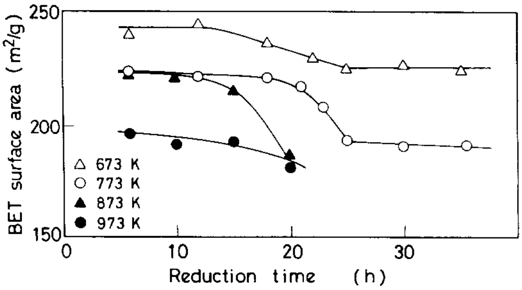

FIG. 4. BET surface area of Ni/PVG at 673, 773, 873, and 973 K.

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